DISTRIBUTION OF SUBSTANCES IN SYSTEMS
WITH A FREE AND A "BOUND" SOLVENT

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16. Abstract

The distribution of caffeine between water and organic solvents (chloroform, dichloroethane) was studied over a wide range of concentrations and temperatures. The ratios of analytically determined compound concentrations, changes in entropy, enthalpy, isobaric and isothermal potential were calculated for the use of free and carrier adsorbed solvents. The activity of the caffeine was greater when "bound" solvents were used than when using free solvents. The difference in the changes in isobaric and isothermal potential for free and "bound" organic solvents serves as a measure of the extent to which the solvent is bound.

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A solvent which is applied to any kind of carrier participates in various chromatographic processes. Its interaction with the carrier should have a substantial influence on the state of such a solvent.

The process of interaction between a carrier and a solvent with the swelling of the carrier, consists of two stages: 1) solvation of the carrier by the solvent, and 2) osmotic penetration of the solvent into the swollen granule. (In the following we will call the solvent which participates in the solvation of a carrier, solvate, while the solvent which enters the granule of a swollen carrier by osmotic penetration is called osmotic.)   /667*

It can be hypothesized that the dissolving action of the solvent which is applied to the carrier will be less than for a solvent in the free[1] state.

In the process of distributing a substance between two solvents, one of which is applied to a carrier, the distribution coefficient[2] of the substance between these two solvents changes as the result of a reduction in the solvent power of the bound solvent. Thus, to calculate the distribution in such systems it is essential to have distributions coefficients measured so as to take into account the interaction of the solvent with the carrier.

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* Numbers in the margin indicate pagination in the foreign text.

[1] In the following, the usual state of the solvent is termed free, while the state of a solvent which is applied to a carrier is called "bound."

[2] Here and in the following, the distribution coefficient is understood to be the ratio of the analytically determined concentrations.

The purpose of the present article is to clarify the character of the change in the distribution coefficients of a substance between two solvents, one of which is applied to a carrier, and to compare them with the distribution coefficients determined between these same solvents in a free state over a wide range of concentrations and temperatures.

Experimental Section

In this work we used a styrene copolymer with 3% divinylbenzene as the organic solvent carrier, which in our previous work was used to separate the substances by the method of inverse partition chromatography, and to create solid organic extractants when isolating substances using counterflow extraction [1-3].

In solving the given problem, the distribution coefficients of caffeine were determined between water and chloroform, water and dichloroethane at 20, 37 and 50° C. The derivation of organic solvents in the bound state using copolymers has been described earlier [2].

It can be seen from Fig. 1 that all three isotherms for the <u>/668</u> distribution of caffeine between water and chloroform are nonlinear in the free state, however, a tendency for them to straighten out is observed with an increase in temperature. When chloroform is used in the bound state, the same tendency of the isotherms to straighten out is observed for an increase in temperature, however, in this case the isotherms are more bent.

To clarify the causes of isotherm bending, the distribution constants, K_o, as defined by the equation

$$K_o = c_2 \gamma_2 / c_1 \gamma_1 = K(\gamma_2 / \gamma_1),$$

were found, where c_1 and c_2 are the molar concentrations of the distributed substance in the aqueous and organic phases, γ_1 and γ_2 are the activity coefficients of the distributed substance in aqueous and organic phases, K is the distribution coefficient.
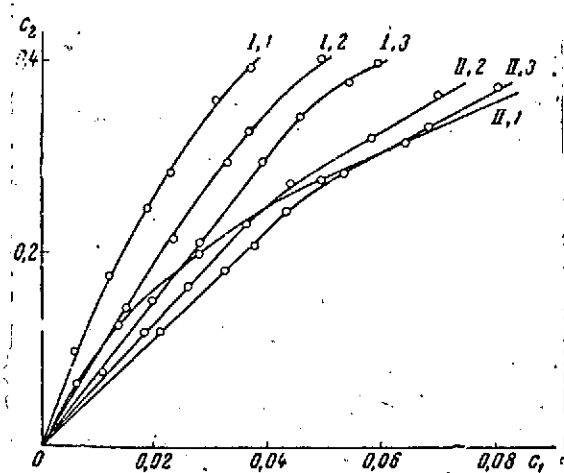
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Figure 1. Isotherms of the caffeine distribution between water and chloroform at different temperatures: I -- free solvent, II -- "bound" solvent; I,1 -- 20° C; I,2 -- 37° C; I,3 -- 50° C; II,1 -- 20° C; II,2 -- 37° C; II,3 -- 50° C; c_1 is the caffeine concentration in the water in moles/ltr, c_2 is the caffeine concentration in the organic solvent in moles/ltr.

Insofar as caffein is a weak electrolyte (pK = 13.39) [4], it can be assumed that the activity of caffein in water is equal to the molarity and its activity coefficient, $\gamma_1 = 1$ (in view of the low solution concentrations).

Then

$$K_o = K\gamma_2 \text{ and } \gamma_2 = K_o/K$$

In order to determine K_o, graphs were drawn showing K as a function of c_1, and K_o was determined by extrapolating to the standard state at c = 0. The extrapolation proves to be sufficiently reliable in view of the fact that K is a nearly linear function of c_1. Knowing K_o, the activity coefficients were found. The results obtained are shown in figures 2 and 3.

It is evident from the data presented that the activity coefficient for caffeine in an organic phase is greater than unity and grows in accordance with the increase in caffein concentration in the organic phase. Such a response of the activity coefficients can be explained from the point of view of the theory proposed by Stokes and Robinson [5].

Each caffein molecule is surrounded by a solvate shell, firmly bound to the molecule and consisting of n molecules of organic solvent. These bound solvent molecules are apparently removed from the free solvent. Thus, in step with the increase in caffeine concentration in the organic phase, the number of free solvent molecules should decrease, and in this respect the active caffeine
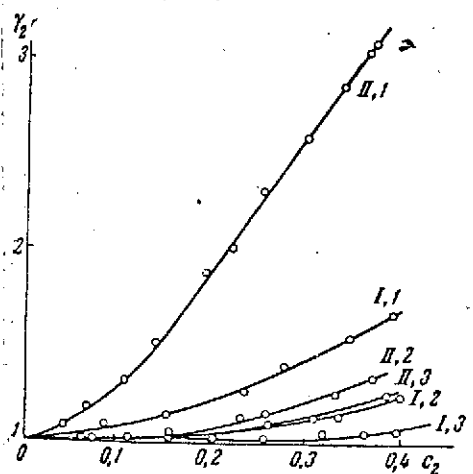
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Figure 2. Activity coefficients of caffeine in chloroform at various temperatures; γ_2 is the activity coefficient of caffeine in an organic solvent. The remaining symbols are the same as for figure 1.
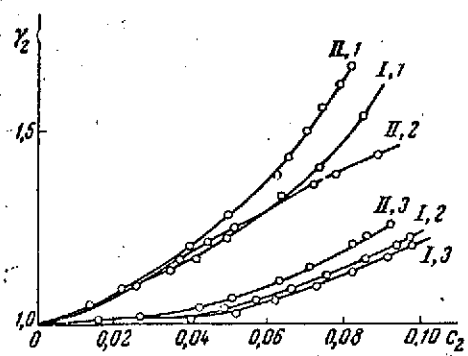

Figure 3. Activity coefficients of caffeine in dichloroethane at various temperatures. The symbols are the same as figures 1 and 2.

should increase and be more analytically determinable. This is confirmed by the increase in the activity coefficients in step with the increase in the caffeine concentration in the organic solvent.

With an increase in temperature, caffeine solvation by the organic solvent decreases, and for this reason the decrease in the number of molecules of the free solvent is not so markedly reflected in the active caffeine concentration in the organic solvent, especially at low caffeine concentrations, which finds expression in the magnitudes of the activity coefficients. In this respect, the caffeine distribution isotherms straighten out with an increase in temperature.

It is evident from the data given /669 in tables 1 and 2 that over the range of temperatures investigated, the caffeine distribution coefficients for the free solvent are greater than for the bound solvent. This shows that the solvent power of the "bound" solvent decreases with respect to the caffeine. By contrasting the distribution isotherms with one another, it is evident that in the initial section the difference is small

and increases with an increase in the concentration in an aqueous solution. This can be explained by the presence of a solvate and osmotic solvent in the swollen granule, based on the hypothesis that the solvate solvent does not participate (or only participates to a quite insignificant extent) in the caffeine dissolution, and all

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the caffeine is dissolved in the osmotic solvent. Thus, with an increase in the caffeine concentration using a bound solvent, the decrease in the number of molecules of the free solvent takes place not only because of the solvation of caffeine molecules by chloroform molecules, but also because of the constant extent of solvationiby the chloroform molecules of the carrier material. For this

TABLE 1

DISTRIBUTION COEFFICIENTS OF CAFFEINE BETWEEN WATER AND CHLOROFORM

c_i, моль/л mole/1	20°C		37°C		50°C		c_i, моль/л mole/1	20°C		37°C		50°C	
	I*	II	I	II	I	II		I*	II	I	II	I.	II
0,005149	17,2	12,2	10,0	7,0	8,0	6,0	0,04634	—	5,8	8,6	6,1	7,8	5,6
0,01023	16,4	11,0	10,1	7,2	7,9	6,0	0,05149	—	5,5	—	5,9	7,6	5,5
0,01545	14,2	9,4	10,1	7,3	7,8	6,0	0,05664	—	5,3	—	5,8	7,4	5,4
0,02060	13,5	8,4	10,1	7,2	7,8	6,0	0,06179	—	5,2	—	5,6	—	5,2
0,02574	12,6	7,5	9,6	6,9	7,8	6,0	0,06693	—	5,0	—	5,5	—	5,1
0,03089	11,8	7,0	9,3	6,6	7,8	6,0	0,07208	—	4,8	—	5,3	—	5,0
0,03604	11,1	6,5	9,1	6,4	7,8	5,9	0,07723	—	4,7	—	—	—	4,9
0,04119	—	6,1	8,9	6,2	7,7	5,8	0,08238	—	4,5	—	—	—	4,8

* I -- free solvent, II -- "bound" solvent

reason the active caffeine concentration in bound chloroform for the same analytically determined concentration is greater than in free chloroform. This is also reflected in the large magnitude of the activity coefficient of caffeine in bound chloroform. /670

TABLE 2

DISTRIBUTION COEFFICIENTS OF CAFFEINE
BETWEEN WATER AND DICHLOROETHANE

c_i, моль/л mole/1	20 °C		37 °C		50 °C		c_i, моль/л mole/1	20 °C		37 °C		50°C	
	I	II	I	II	I	II		I	II	I	II	I	II
0,005149	2,50	2,00	2,50	2,00	2,70	2,40	0,04119	1,85	1,50	2,22	1,56	2,32	1,91
0,01023	2,40	2,00	2,50	2,00	2,75	2,30	0,04634	1,75	1,44	2,17	1,53	2,26	1,86
0,01545	2,28	1,86	2,56	1,86	2,76	2,30	0,05149	1,68	1,37	—	1,50	—	1,83
0,02060	2,19	1,77	2,55	1,77	2,75	2,20	0,05664	1,60	1,32	—	1,45	—	—
0,02574	2,08	1,70	2,44	1,70	2,56	2,14	0,06179	—	1,27	—	1,42	—	—
0,03089	2,00	1,61	2,36	1,66	2,48	2,05	0,06693	—	1,24	—	—	—	—
0,03604	1,93	1.56	2,28	1,61	2,40	1,97							

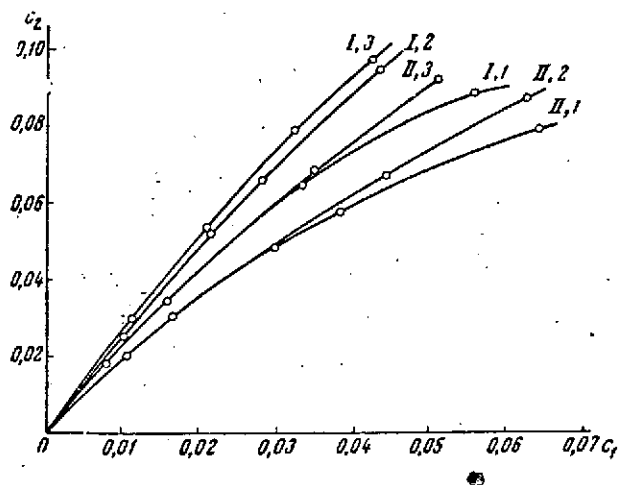Small differences in the course of the isotherms in the initial

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Figure 4. Distribution isotherms of caffeine between water and dichloroethane at various temperatures. The symbols are the same as in figure 1.

sections is explained by the fact that for small caffeine concentrations in chloroform, the presence of a solvate solvent does not have a substantial effect on the magnitude of the active caffeine concentration.

With an increase in temperature, all changes during the use of a free and a "bound" solvent are analogous.

The ratio of the thermodynamic distribution constants K_o, where free and "bound" solvents are used at a given temperature, shows that portion of the solvent which does not take part in the distribution process. The constancy of the ratios during changes in temperature shows that solvation of the carrier material by an organic solvent practically does not change under the given conditions. This is confirmed by the invariability in the degree of swelling of the copolymers within this temperature range.

The results obtained in experiments on the distribution of caffeine between water and dichloroethane are in many respects analogous to the results obtained during the distribution between water and chloroform. The somewhat different disposition of the distribution isotherms (figure 4) when using dichloroethane is /671 connected with the difference in the influence of temperature on the solubility caffeine in chloroform and dichloroethane.

It is evident from the data given in table 2 that the distribution coefficients differ in absolute magnitude less when using free and "bound" dichloroethane, than when using chloroform.

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This attests to the somewhat different interaction of dichloro-
ethane with the copolymer. In all probability there is more os-
motic solvent in the copolymer granule, swollen in dichloroethane,
than in the copolymer granule swollen in chloroform, and conse-
quently there is less solvate solvent which does not take part in
the distribution process when dichloroethane is used, than in the
case where chloroform is employed. This is also confirmed by the
smaller difference in distribution coefficients of caffeine between
free and "bound" dichloroethane.

However, it can be hypothesized that the difference in the
caffeine distribution coefficients between water and solvents in
free and "bound" states does not attest to the fact that the
"bound" solvent does not take part (or participates, but to an
insignificant extent) in the dissolution process of the caffeine,
but rather to the fact that not all "bound" solvent proves to be
accessible for the caffeine molecules.

A comparison of the extent of utilization of bound chloroform
and dichloroethane refutes this hypothesis. The relative swelling
of the copolymer sample we used in chloroform was 225%, and 150%
in dichloroethane. Consequently, the solvent in the granule which
swells in dichloroethane, in view of the lower porosity of the
granule, should be less accessible for the caffeine molecules than
the solvent in the granule swollen in chloroform. However, the
experimental data indicates the opposite. In the same range of
concentrations of an aqueous caffeine solution, the extent of util-
ization of the chloroform computed from the ratio of caffeine dis-
tribution coefficients between water and solvents in free and
"bound" states, on an average amounts to ≈70%, while the extent
of dichloroethane utilization is 79%.

The given data indicate that when a "bound" solvent is used
there are either no spatial hindrances to the penetration of the
caffeine molecule into the swollen granule, or they are insignif-
icant. This also confirms that the amount of solvate solvent is

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less when using "bound" dichloroethane, than when using "bound" chloroform, and points up the difference in the swelling processes of the copolymer in chloroform and dichloroethane.

We calculated the changes in enthalpy, the isobaric - isothermal potential and entropy for caffeine distribution between water and organic solvents both in the free and the "bound" states. The standard values of thermodynamic functions were calculated in accordance with well-known thermodynamic equations. The results obtained are given in table 3.

TABLE 3

Растворитель Solvent	K_0			ΔH^0, кал cal.	ΔZ^0, кал cal.
	20 °C	37 °C	50 °C		20 °C
$CHCl_3$ (1)	19,00	10,50	8,10	—5350,0	—1715,16
$CHCl_3$ (2)	14,35	7,35	6,10	—5367,0	—1551,52
$C_2H_4Cl_2$ (1)	2,60	2,60	2,80	465,2	— 556,80
$C_2H_4Cl_2$ (2)	2,08	2,08	2,30	629,9	— 426,60

Растворитель Solvent	ΔZ^0, кал cal.		ΔS^0, э. е. e.u.		
	37 °C	50 °C	20 °C	37 °C	50 °C
$CHCl_3$ (1)	—1449,06	—1343,18	—12,40	—12,57	—12,40
$CHCl_3$ (2)	—1229,26	—1161,03	—13,01	—13,34	—13,01
$C_2H_4Cl_2$ (1)	— 588,87	— 661,16	3,48	3,40	3,48
$C_2H_4Cl_2$ (2)	— 451,38	— 534,75	3,60	3,48	3,60

The constancy of the enthalpy variations where free and "bound" solvents are used, shows that the copolymer does not influence the magnitude of the thermal effect of caffeine dissolution in an organic solvent and confirms the fact that caffeine is not adsorbed on the carrier during the distribution of caffeine between water and a "bound" solvent. We arrived at the last conclusion based also on a study of the adsorption capacity of the copolymer [3]. Differences in the changes in enthalpy when using chloroform and dichloroethane attest to the fact that the interaction of caffeine with chloroform is enormously greater than with dichloroethane.

The same entropy changes when the temperature is increased from 20 to 50° C shows that in this range of temperatures the orderliness of the system does not change.

The lower value of entropy with the use of chloroform in comaprison with the use of dichloroethane shows that caffeine has a greater ordering effect when introduced into chloroform, than when introduced into dichloroethane.

Small differences in entropy changes when using "bound" solvents in comparison with the use of free solvents attests to the fact that the presence of the copolymer does not exert a substantial influence on the orderliness of the system.

The variations in the distribution constants, and consequently also variations in the decrease of the isobaric - isothermal potential with an increase in temperature when using chloroform and dichloroethane were determined by the different fluctuations in solubility of caffeine in the indicated solvents.

The reduction in the diminution of the isobaric - isothermal potential when using "bound" solvents, in contrast to the use of free solvents, reflects the decline in the transition of caffeine to a "bound" solvent as a result of a delcine in its solvent power. Thus, the difference in the changes in the isobaric anisothermal potential when using a free and a "bound" solvent can be a measure of the "boundness" of the solvent.

Conclusions

1. The distribution of caffeine between water and organic solvents (chloroform, dichloroethane) was studied over a wide range of concentrations and temperatures. Organic solvents were employed in both free and "bound" states. The reduction in the caffeine distribution constants when using "bound" solvents is explained by the presence of a copolymer of the solvate solvent

in the swollen granule, which does not participate in the distribution.

2. The activity coefficients of caffeine were calculated in the organic phase for its distribution between water and chloroform, water and dichloroethane. The magnitude of the activity coefficient increases with an increase in the caffeine concentration in an organic phase. The values of the activity coefficients when using "bound" solvents are greater than when free solvents are used as a result of a decline in the solvent power of the "bound" solvent. /673

3. Changes in the enthalpy, isobaric - isothermal potential and entropy were calculated for the caffeine distribution using free and "bound" organic solvents. The difference in the variations of the isobaric - isothermal potential for free and "bound" organic solvents can be used as a measure of the "boundness" of the solvent.

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